Standard for measuring Biomethane Potential and the Residual Biogas Production

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innovations in the BIOMETHANE uniVERSE

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Biochemical Methane Potential

What

The biomethane potential or biochemical methane potential (BMP) of a specific substrate defines the maximum amount of methane that can be produced by anaerobic digestion under controlled conditions → Similar to the aerobic BOD but under anaerobic conditions

Why

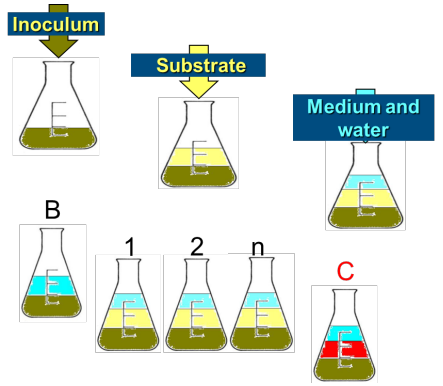
Routinely applied to measure the ultimate methane production from different organic materials under reference conditions (T, mixing, nutrient availability, initial loading, test duration)

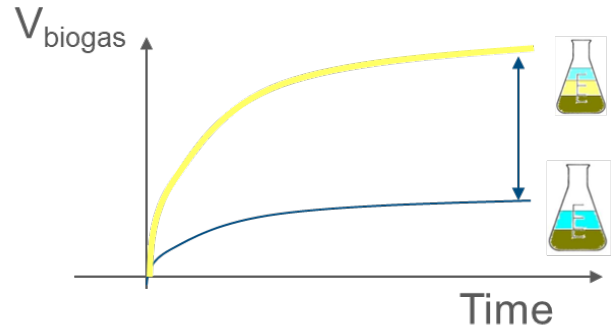
Provides infos for:

- Feedstocks evaluation: expected methane production per unit of volume/weight/DM
- Process evaluation: comparison between expected (BMP) and actual methane production (at plant level)
- Comparison of anaerobic digestion conditions
- Effect of pre-treatments

How

- Feedstock is added to an adequate inoculum → how much, in which proportion, how many replicates, blanks, control … ?
- Environmental conditions are maintained for a minimum test duration → which one
- Methane production is quantified → How? various alternatives are available





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Biochemical Methane Potential

Norms / Standards / Guidelines

- Original protocol: Owen, W. F., Stuckey, D. C., Healy Jr, J. B., Young, L. Y., & McCarty, P. L. (**1979**). Bioassay for monitoring biochemical methane potential and anaerobic toxicity. Water research, 13(6), 485-492.
- Several norms exist since years mainly targeting ultimate degradability of materials, but their formulation of important parameters is often vague.

	DIN 38414 TL8	VDI 4630	ISO 11734	ISO 15985	ISO 14853	ASTM D 5250	ASTM D 5511
Year	1985	2006	1995	2004	2005	1992	1994
Monitored parameter	Biogas	Biogas	Biogas + dissolved inorganic carbon	Biogas + organic caron	CO2, CH4 , COD, total/dissolved inorganic carbon. (biomass growth)	CO2, CH4, COD, soluble organic carbon, polymers	Biogas, CH4 , COD
Tested material		Organic material	Soluble organics	Organics with high DM	Powdered/solid organics	Plastics	Plastics
Mineral medium	None, possible supplementation of NH4Cl, NaH2PO4 to adjust C:N:P to100:6:1	None	Phosphate buffer, mineral medium	None	Phosphate buffer, mineral medium	Phosphate buffer, mineral medium	None
Temperature	35± 1	37± 2 or 55 ± 1	35± 2	52± 2	35± 2	35± 2	52± 2
Volume	500 mL	500, 1000 o 2000 mL	100-1000 mL	> 750 mL	250 mL	100 mL	1000 mL
Vitamins	No	No	No	No	Yes (optional)	No	No
Trace elements	No	No	Yes (optional)	No	No	Sì	No

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Biochemical Methane Potential

Norms / Standards / Guidelines

	DIN 38414 TL8	VDI 4630	ISO 11734	ISO 15985	ISO 14853	ASTM D 5250	ASTM D 5511
Inoculum origin	Digestate from WWTP	Digestate from WWTP or agri-AD	Digestate from WWTP	Digestate from thermophilic digestion f biowaste	Digestate from WWTP	Digestate from WWTP	Digestate from WWTP (thermophilic)
Inoculum pretreatment		Pre-incubation for 7 d, (washing)	Washing, Pre-incubation	Pre-incubation	Whashing with phosphate buffer	Pre-incubation (7-14 d)	Pre-incubation (7 d)
Test duration	20-40 d	Till < 1% criterion	60 d	15 d	60 d		Till degradation of 70% for reference substrate
Gas measurement	Volumetric	Manometric/ Volumetric	Manometric/ Volumetric	Volumetric	Manometric/ Volumetric	Manometric/ Volumetric	Volumetric

The **need for harmonization** motivated various efforts from technical groups:

- 'Task Group for the Anaerobic Biodegradation, Activity and Inhibition of the Anaerobic Digestion Specialist Group of the International Water Association (**IWA ABAI-Group**)
- From 2002 → scientific reviews including protocol that defines the BMP of solid organic wastes and energy crops in batch assays (Angelidaki et al. 2009).
- **Association of German Engineers**: technical guideline **VDI 4630 -2006** 'Fermentation of organic materials. Characterization of the substrate, sampling, collection of material data, fermentation tests' updated version (**VDI 4630 2016**).
- EPFL/Aarhus/TUM working group – Protocol + 2 ring tests (Holliger, et al. 2016; Hafner et al., 2020)

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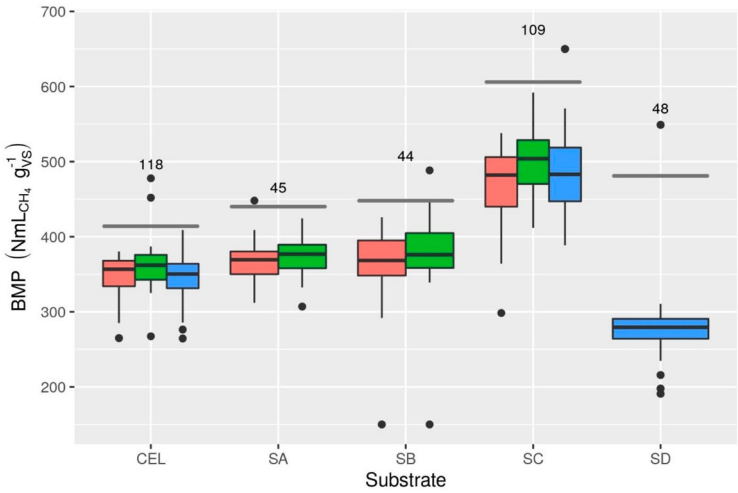
Biochemical Methane Potential

Ring tests

	Raposo et al., 2011 (CSIC)	Cresson et al., 2015 (French study)	Holliger et al., 2020 EPFL, Aarhus, TUM (2015-2018)	
Substrate	S1:starch, S2: cellulose, S3: gelatine, S4: mung bean	S1: Potato+ Grain+ maize+ Beef +Wheat straw S2: Wheat straw S3: Mayonnaise	2X (SA, SB, SC = Complex mixture of commercial animal feed + Cellulose)	SC, SD (Wheat straw)+ Cellulose
I/S	1 and 2	Free and 2	Fixed	Fixed (multiple)
Operational conditions	Free	Free	Protocol in Holliger et al., 2016 **(*)**	Protocol in Holliger et al., 2016; (but: sieving ok, mass of substrate > 1 gVS; no restriction on total VS, T [35-40°C]± 1) 2X inoculum source
Inoculum source	Free	Free		
N of participants	19	11	31	37
reproducibility relative standard deviation	15-37%	13-21%	7.5-24% Reduced to 8% using validation criterion on cellulose	7.7-17%

(*) Protocol

- Inoculum : VS = 15 and 40 $g \cdot L^{-1}$, pH = 7.0 - 8.5, VFA < 1.0 $g \cdot L^{-1}$, TAN < 2.5 $g \cdot L^{-1}$, alkalinity > 3 g $CaCO_3 \cdot L^{-1}$, No Sieving, storage (at ambient or test temperature) ≤ 5 days.
- Substrate >2 g per bottle,
- trace element and vitamin solutions
- Total VS = 20 - 60 $g \cdot L^{-1}$.
- Headspace flushed with N_2 +CO_2 or N_2
- Temperature = 35 ± 2 °C
- Tests duration according to 1% criterion



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Biochemical Methane Potential

Ring tests EPFL, Aarhus, TUM (2015-2018) – take home message

Main source of variability:
From literature: almost everything affects results!!

Main factors after large ring-testing:
- Inoculum (source, storage, dilution): relevant to kinetics but not significantly to BMP. De-gasing not so influential (additivity blank + substrate was confirmed over reasonable ranges)
- I/S: not relevant if adequate
- Measuring principle and apparatus (especially as for manual manometric, volumetric equipment → gas losses → gravimetric check may be useful) and data processing (e.g. water vapor, initial Headspace composition),

Importance of validation criteria:
- Triplicate bottles for blanks and substrate bottles
- Positive control (cellulose) with BMP included between 340 and 395 NmLCH4/gVS and RSD < 6% (including blank, sample and VS)
- Termination of tests only when net daily methane production during three consecutive days is <1% of the accumulated volume of methane

→ Half of the BMP values in the large ring tests were not validated, but final interlaboratory RSD was deuced to 8%

https://www.dbfz.de/en/projects/bmp/methods

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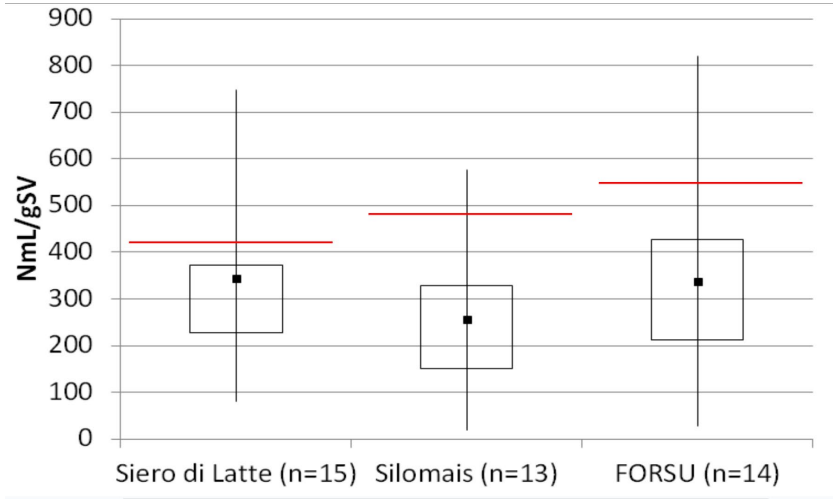
Biochemical Methane Potential

Norms / Standards / Guidelines

- Italian ring test (2013) organized by Fabbrica della Bioenergia - POLIMI

	Fabbrica della Bioenergia (2013)
Substrate	cheese whey, corn silage, OFMSW
I/S	2
Operational conditions	T > 30°C
Inoculum source	Free
N of participants	19
Reproducibility relative standard deviation (RSD)	RSD > 170%, after outliers' removal according to UNI5725 RSD = 40-170%)



- Strong need for guidelines → CTI launched a working group (2015-2018) that eventually issued the Italian technical standard **UNI/TS 11703:2018**

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Residual Biogas Potential

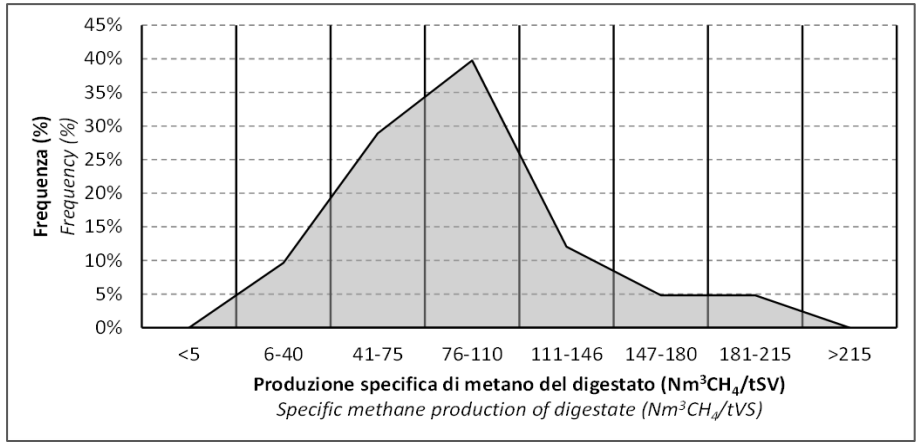
What

The residual biogas potential (RBP) of digestate defines the amount of biogas that could still be produced from the organic material present at the end of the anaerobic digestion.

Why

Provides infos for:

- evaluation of biological efficiency (at plant level)
- Stability criteria REGULATION (EU) 2019/1009
- a starting point to carry out mathematical modeling to calculate methane emissions from storage tank

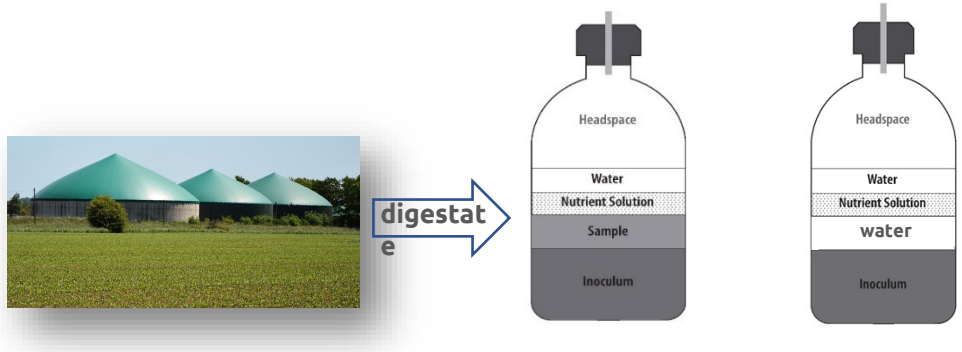


CRPA data about 300 digestate sampled from 80 different biogas plants

How

Standardized method is in progress (CEN/TC 223/WG 4)

- Batch test
- Digestate is added to an adequate inoculum → how much, in which proportion, how many replicates, blanks, control … ?
- Duration test: 28 d
- Biogas/Methane production is quantified → Manometric/Volumetric



Glass or steel gastight vessels (with a volume of 0,5 l to 2,5 l)

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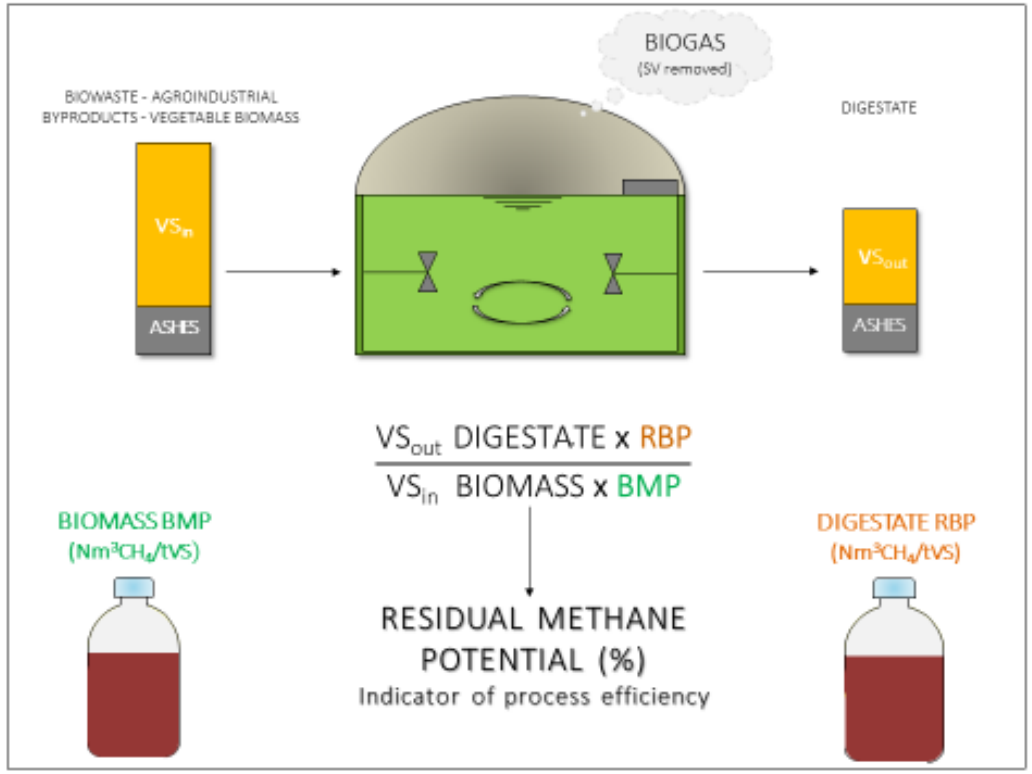
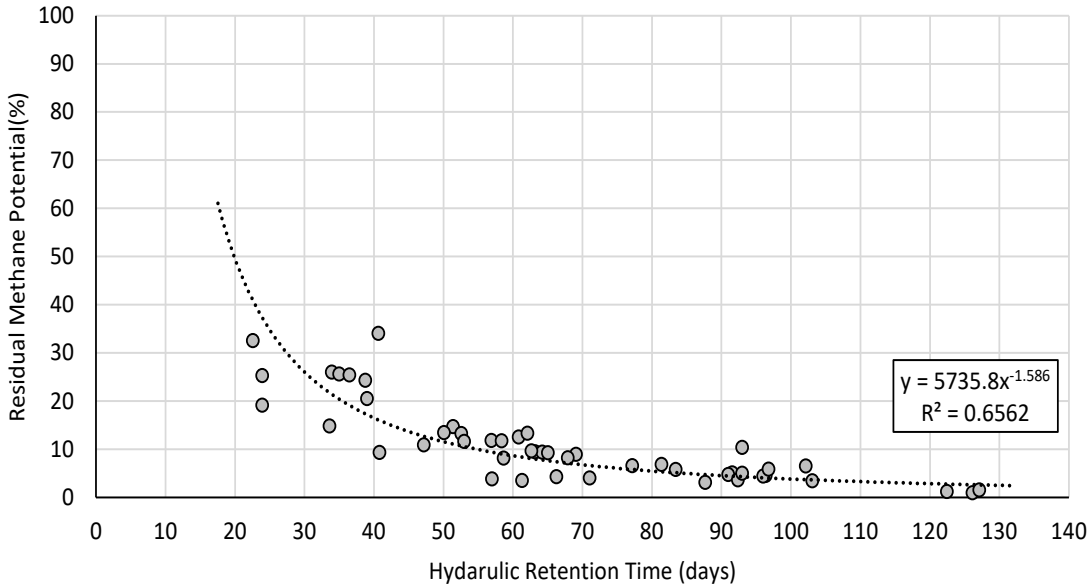
Residual Biogas Potential

Provides infos for:

- The comparison between the specific residual methane production of the digestate (RBP – Residual Biogas Potential) and the specific methane production of the biomasses at loading (BMP – Biochemical Methane Potential) allows the calculation of the residual methane potential as an indicator of the efficiency of the process.





Distribution of the Hydraulic Retention Time (HRT) and the Residual Methane Potential (RMP) of biogas plants.

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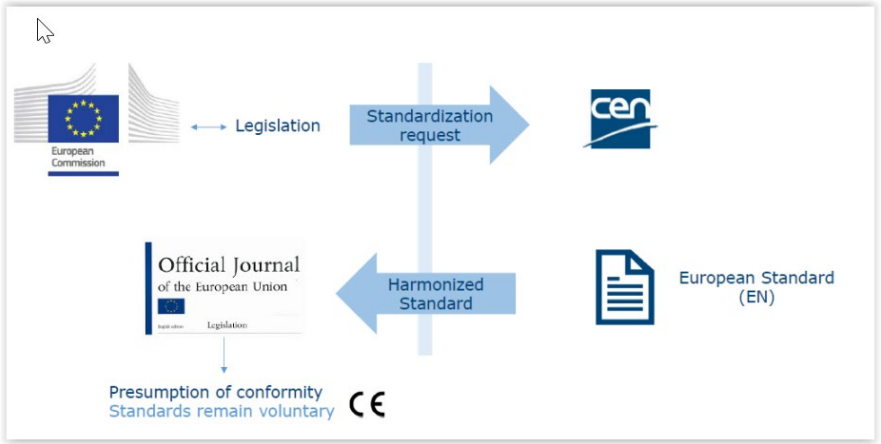
Residual Biogas Potential

Norms / Standards / Guidelines

- With Standardization Request (SReq) M/564 of February 2020, the European Commission (EC) charged the European Committee for Standardization (CEN) to elaborate harmonized European Standards and European standardization deliverables in the framework of the Regulation (EU) 2019/1009 on fertilizers .



Component Material Categories CMC
CMC 4: FRESH CROP DIGESTATE
CMC 5: DIGESTATE OTHER THAN FRESH CROP DIGESTATE

REGULATIONS

REGULATION (EU) 2019/1009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 5 June 2019

laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003

6. Both the solid and the liquid part of the digestate shall meet at least one of the following stability criteria:

(a) Oxygen uptake rate:

— Definition: an indicator of the extent to which biodegradable organic matter is being broken down within a specified time period. The method is not suitable for material with a content of particle sizes > 10 mm that exceeds 20 %.

— Criterion: maximum 25 mmol O_2/kg organic matter/h; or

(b) Residual biogas potential:

— Definition: an indicator of the gas released from a digestate in a 28 day period and measured against the volatile solids contained within the sample. The test is run in triplicate, and the average result is used to demonstrate compliance with the criterion. The volatile solids are those solids in a sample of material that are lost on ignition of the dry solids at 550 °C.

— Criterion: maximum 0,25 l biogas/g volatile solids.

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Residual Methane Potential

Norms / Standards / Guidelines

- CRPA project leader for method**: Digestate – Determination of the residual biogas potential.**
- Present stage: drafting of 1st working document; circulation of 1st WD; Next stage: consensus and consolidation; acceptance of ENQ draft

- CRPA is responsible of the Interlaboratory study in 2024 performed in order to determine the applicability and precision of this analytical methods.

	General guidelines
Sample	Digestate, solid fraction digestate
I/S	2
Operational conditions	T = 38°C ± 2 °C
Inoculum source	Free
N of participants	Minimum 8
Measurements method	Manometric/Volumetric

- The execution of the activities of CEN/TC 223lly are seconded to the Royal Netherlands Standardization Institute (NEN)
- the CRPA coordinates the interlaboratory test
- ILVO, Belgium, institute responsible of sampling and preparation of samples
- The statistical analysis will be performed by AGES Institute Wien

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Specific Hydrogenotrophic Methanogenic Activity

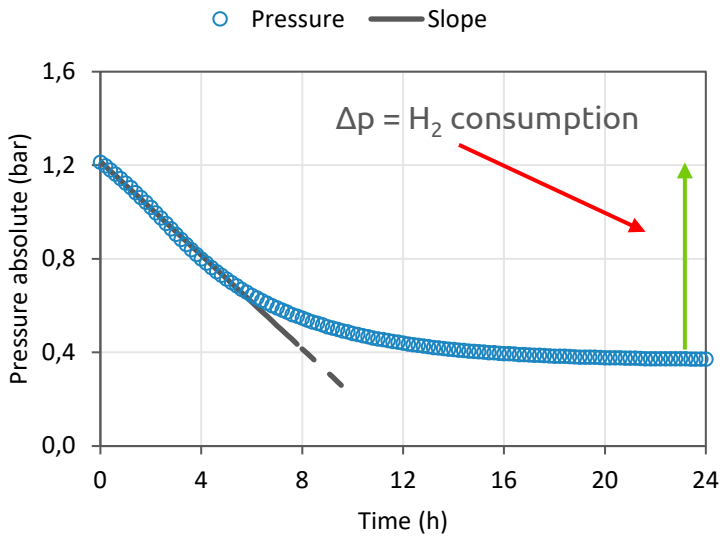
What?

SHMA is the measure of the **rate** of H_2 consumption [mL_N CH_4/(g VSS·d)]

Why?

Increasing interest for research and full-scale applications:

- Optimizing start-up procedures
- Technical testing of H_2 gas-liquid mass transfer
- Comparison between SHMA and the activity in a full-scale operating plant

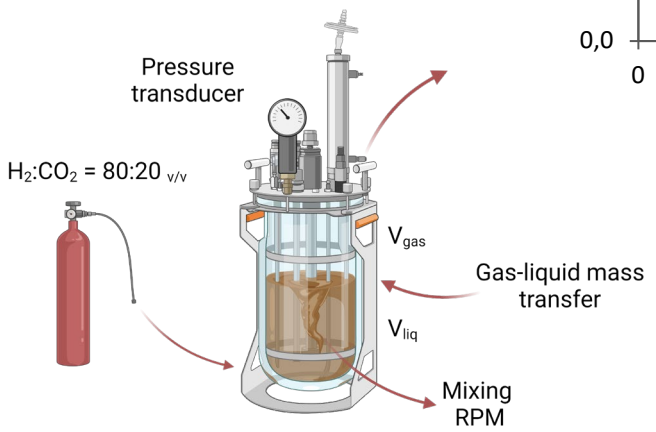


How?

Batch manometric methods:

- Coates et al., 1996
- Ripoll et al., 2020

$$SHMA = \max\left(\frac{\Delta p}{\Delta t} \cdot \frac{V_{gas} \cdot VM \cdot s}{VS \cdot R \cdot T_{op}}\right)$$



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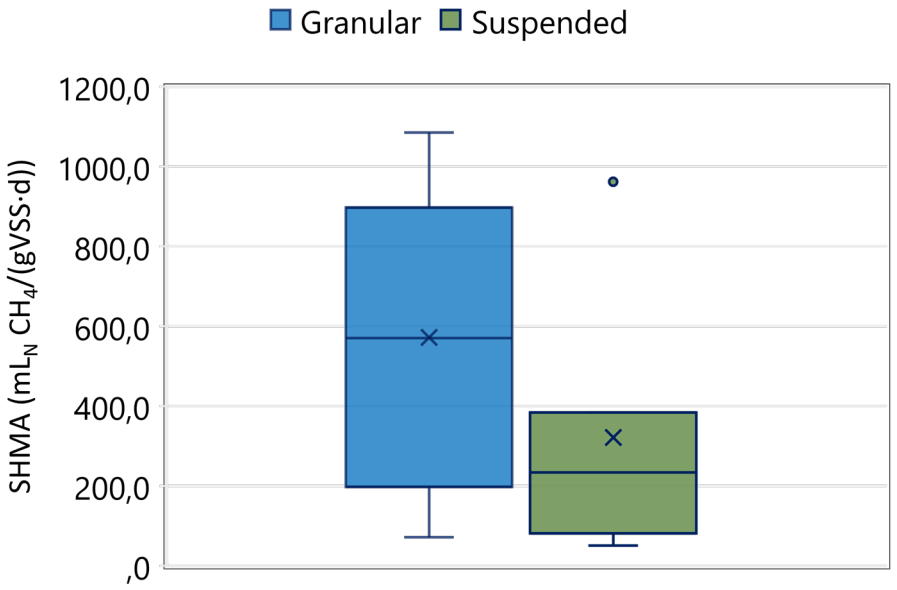
Specific Hydrogenotrophic Methanogenic Activity

Ring test promoted by Prof. Borzacconi in 2021

Participants:

1) Politecnico di Milano
2) Universidad de la República de Uruguay
3) Technical University of Denmark (DTU)
4) Minho University
5) Aarhus University
6) ELGO University
7) BioProcess control (now BCP Instruments AB)

General guidelines	
Substrate	Mixture of H_2:CO_2 (80:20)
I/S	1
Operational conditions (mixing and initial pressure)	Free
Temperature	37 °C ± 2 °C
Inoculum source	• Mesophilic granular sludge from a paper mill • Mesophilic suspended sewage sludge
Measurements method	Manometric/Volumetric



High CV for both inoculum:

- 62% granular sludge
- 96% suspended sludge

Need of a standardized method!!

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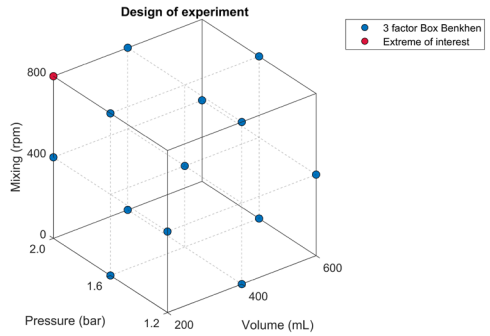
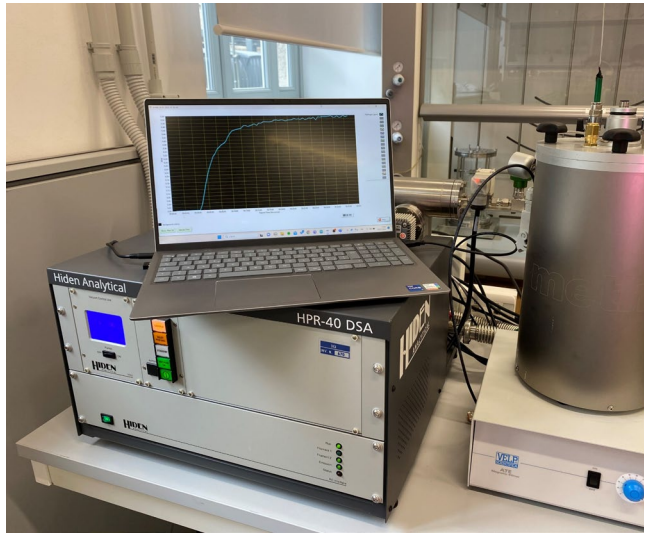
Specific Hydrogenotrophic Methanogenic Activity

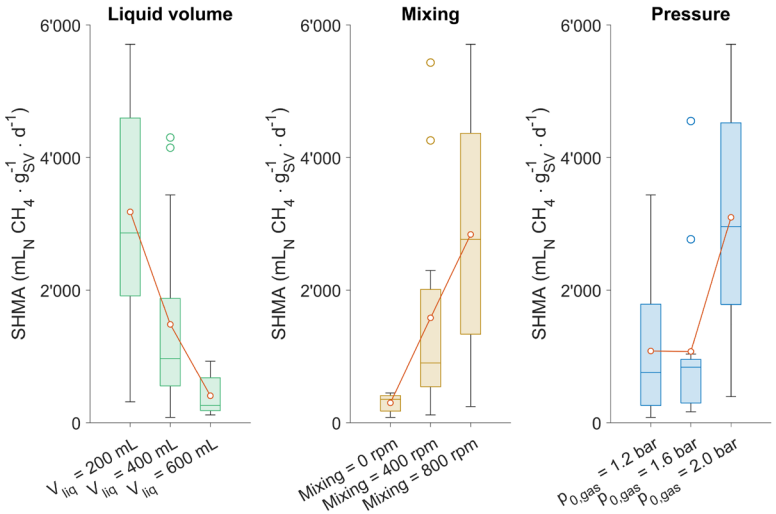
Evaluations on the role of operating conditions

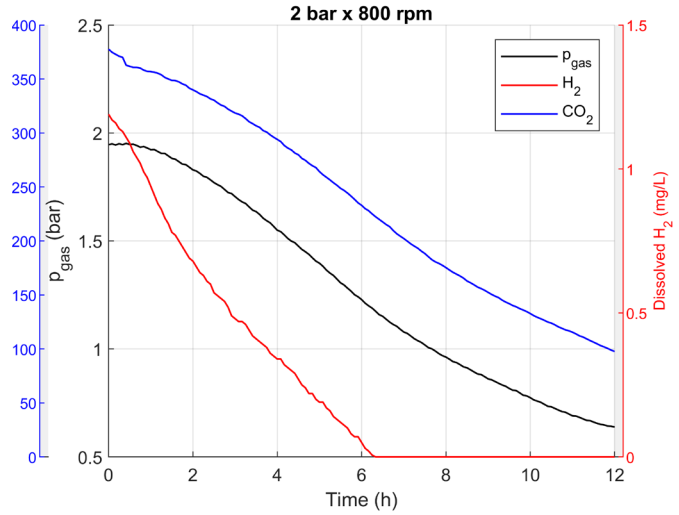
1. Operating conditions tested:
   a) Initial H_2 partial pressure [1.2-1.6-2.0] bar;
   b) Mixing [0-400-800] rpm;
   c) Liquid volume ratio (V_{liq}/V_{tot}) [0.05-0.10-0.15]

2. Dissolved H_2 concentration during the test









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